

ATTACHMENT

PATENT ABSTRACTS OF JAPAN

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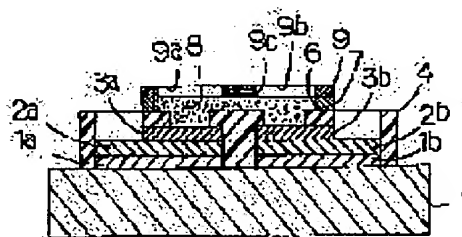
(54) CHEMICAL SENSOR AND MANUFACTURE OF SENSOR PLATE

(57)Abstract:

PURPOSE: To reduce an irregularity in the shape of a membrane when a chemically responsive membrane is formed and to reduce an irregularity in an output by a method wherein the chemically responsive membrane is formed by dropping a material for the chemically responsive membrane and its surface is leveled by executing a heating treatment.

CONSTITUTION: Silver layers 2a, 2b are left, as contact parts for a probe, on silver chloride layers 3a, 3b, and an insulating film 4 is formed. Electrodes and both end sides of the insulating film 4 are left, and a bank body 7 having a slender hole 6 is formed on the insulating film 4.

Then, a tetrahydrofuran solution which contains sodium ionophore, orthonitrophenyl octylether as a membrane solvent and a vinyl chloride copolymer as a carrier is dropped into the slender hole 6, the solvent is volatilized at room temperature and in the air, and a sodium-ion responsive membrane 8 is formed. A sodium-ion sensor plate component which is obtained is put into an oven, and the sodium-ion responsive membrane 8 is melted. After that, the membrane is taken out from the oven so as to be cooled spontaneously, and the sodium-ion responsive membrane 8 is regenerated.



DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the manufacture approach of the sensor plate of the chemical sensor which measures the ion concentration of specimen liquid, such as blood, and its component.

[0002]

[Description of the Prior Art] In order to measure the ion concentration of specimen liquid, such as blood In the condition of having prepared by making into a pair the specimen liquid measuring electrode and the reference electrode in which the ion sensing membrane was formed on the substrate, having covered by the insulator layer so that a window part might be formed in the tip side of these electrodes, and criteria liquid and specimen liquid having been dropped at these window parts, and having made it the ion conductive state The so-called differential formula ion sensor which connects each electrode to a measuring circuit and measures the potential difference based on the concentration difference of criteria liquid and specimen liquid is known.

[0003] In order to have manufactured this ion sensor, as it proposed by previous application, it etches into the electric conduction pattern of the predetermined configuration which consists of what estranged the strip of the piece of copper by the photolithographic method etc., compared the so-called printed-circuit board, has arranged in the condition, and was made into the pair which stuck copper foil with a thickness of 35 micrometers on the paper polyester insulating substrate, and mirror polishing of the front face of the piece of copper of that pattern is carried out if needed. Subsequently, electrolytic plating is carried out using a commercial gloss silver plating bath, and an about 10-15-micrometer silver larer is formed. Furthermore, it is immersed into the solution of hydrochloric acid, and a several micrometers silver chloride layer is formed in a silver larer front face by carrying out electrolytic formation processing.

[0004] Next, it leaves a part of each edge where a pair each of silver chloride layers face, a front face is covered with the insulator layer which consists of resin, such as an epoxy resin, and a window part is formed. It leaves the window part and the meantime which make these pairs, the thin long hole corresponding to this is formed, and a levee body is further formed on an insulator layer. And the thin long hole containing the above-mentioned window part is made to trickle and dry the ion induction ingredient solution containing the macrocyclic compound called an ionophore, ion exchange resin, etc., and an ion sensing membrane is formed on the silver chloride layer of a window part. Thus, after forming the above-mentioned silver chloride layer, the approach of forming an ion sensing membrane only in the need part of a silver chloride layer has the advantage that there is little futility, by not using many expensive ingredients, such as an ionophore, rather than it forms an ion sensing membrane in the whole like the above.

[0005]

[Problem(s) to be Solved by the Invention] However, in case an ion induction ingredient solution is dropped and that spreading film is formed on the silver chloride layer of a window part, it carries out by leaving desiccation of this spreading film in the ordinary temperature in atmospheric air, and when a solvent volatilizes, it is carrying out. Therefore, the volatilization rate of a solvent was not too quick, and the volatilization rate of a solvent was not fixed in the situation of perimeters, such as ambient temperature, and variation arose in the thickness of a dry paint film, and by the ion sensor using this as an ion sensing membrane, variation arose in the output potential, and when the substandard thing was used as the defective, it had become the cause of a yield fall.

[0006] In case the purpose of this invention forms the chemistry induction film by dropping a chemistry induction film ingredient solution only at a required part, it lessens variation in a film configuration, and it is to offer few chemical sensors and sensor plates of variation of an output.

[0007]

[Means for Solving the Problem] In the manufacture approach of the chemical sensor which makes a

pair the specimen liquid measuring electrode which covered the chemistry induction film, and a reference electrode, prepares at least 1 set, and enabled it to measure the concentration of the specific object of specimen liquid in order that this invention might solve the above-mentioned technical problem or [leaving that spreading film in the solvent ambient atmosphere which makes this chemistry induction film dissolve or swell by forming the above-mentioned chemistry induction film by dropping of the solution of this chemistry induction film ingredient] -- or the manufacture approach of the chemical sensor to heat-treat is offered.

[0008] or [moreover, / leaving / in the manufacture approach of a sensor plate of having made into the pair the specimen liquid measuring electrode which covered the chemistry induction film, and the reference electrode, and having prepared the lot on the substrate at least / that spreading film in the solvent ambient atmosphere which makes this chemistry induction film dissolve or swell by forming the above-mentioned chemistry induction film by dropping of the solution of this chemistry induction film ingredient] -- or the manufacture approach of the sensor plate heat-treat offers.

[0009] Under the present circumstances, the solvent made to dissolve or swell is the same solvent as a chemistry induction film ingredient solution, and, as for heat-treatment, it is desirable that it is more than the glass transition temperature of the chemistry induction film.

[0010]

[Function] if the chemistry induction film which trickled the chemistry induction film ingredient solution, was made to leave in ordinary temperature atmospheric air, and was made to season naturally is left in the dissolution or a swelling solvent ambient atmosphere, the film will dissolve or swell -- flowing -- being easy -- since volatilization of the solvent is controllable slowly -- a front face -- ***** -- things are made. Moreover, since the chemistry induction film is softened, it becomes easy to flow by heat-treating and Control of the cooling rate can be carried out, a front face is ** carried out. Thus, equalization of a film configuration is made.

[0011]

[Example] Next, the example of this invention is explained based on a drawing. First, as shown in drawing 1 and 2, patterning of the copper foil pasted up on the paper polyester substrate 1 was carried out by the photolithographic method, it ground to the mirror plane by the 2-micrometer diamond slurry, and the copper electrodes 1a and 1b of the predetermined configuration which estranged and compared ***** and has been arranged in the condition were formed.

[0012] Next, it rinsed, after performing cleaning by the commercial degreaser, and cathode electrolytic degreasing. It was immersed holding after this at the temperature of 30 degrees C in commercial gloss silver plating liquid (the product made from Japanese High grade Chemistry, the JPC TEMPERE resist AGR (2)), electrolysis plating was performed for 2 minutes and 30 seconds by having made a platinum plating titanium mesh into the anode plate by cathode-current-density 10 A/dm² (ampere per unit decimeter), and silver larer 2a and 2b with a thickness of 10-15 micrometers were formed.

[0013] After masking so that the contact surface connected with output circuit equipment may not be silver-chloride-ized, then, in the hydrochloric acid of a decinormal Use an operation pole and a platinum electrode into a counter electrode, and a silver-silver chloride electrode is used as a reference electrode for the electrode in which the above-mentioned silver larer was formed. After holding for 60 seconds in initial potential of 80mV using a potentiostat and a function generator, An initial sweep direction is made into the direction of a cathode, a sweep is carried out to -1500mV, a sweep is carried out by trace-speed 50 mV/sec to 80mV of clinches, 5 cycle sweep of for 150mV subtracted from 350mV is carried out by trace-speed 20 mV/sec after that, and the silver chloride layer of a particle is formed preparatorily. This electrode that formed the silver chloride layer preparatorily was used as cathode in the hydrochloric acid of a decinormal after that, electrolytic formation processing of an anode plate and the platinum plating titanium mesh was carried out for 2 minutes and 40 seconds by anodic current-density 0.23 A/dm² (ampere per unit DESHI square meter), and the silver chloride layers 3a and 3b were formed on the edge where above-mentioned silver larer 2a and 2b face. Thus, the normal electrode which consists of 1a, 2a, and 3a, and the specimen liquid measuring electrode which consists of 1b, 2b, and 3b are formed.

[0014] It leaves a part of edge approach on above-mentioned silver chloride layer 3a and 3b which faces, and exposed above-mentioned silver larer 2a and 2b as a contact surface of a probe, and an insulator layer 4 is formed with an epoxy resin, a crevice is formed in the former, it leaves a part for the both-ends flank of an electrode and an insulator layer 4 further to this insulator layer 4 between these crevices and these, and the levee body 7 which has the thin long hole 6 corresponding to the former is formed.

[0015] The tetrahydrofuran (THF) solution containing the vinyl chloride copolymer which is the alt.nitrophenyl octyl ether (o-NPOE) and support which are Bis (12 - CROWN- 4) and the film solvent which are a sodium ionophore was dropped in the above-mentioned thin long hole 6, the solvent was volatilized in ordinary temperature and atmospheric air, and the sodium ion sensing membrane 8 was formed. Thus, sodium sensor plate components are done.

[0016] Next, into the well-closed container with a cock, THF is made into constant-rate ON **, and the inside of a container is made into the THF saturation ambient atmosphere. Opening the cock of a container, after it held the sodium sensor plate components in which the above-mentioned ion sensing membrane 8 was formed into this and the sodium ion sensing membrane fully dissolved, THF was vaporized gradually and the ion sensing membrane was slowly reproduced over 2 hours or more.

[0017] Thus, the photograph of the obtained sodium ion sensing membrane front face is shown in drawing 3 . This photograph shows that there is no local irregularity in a sodium ion sensing membrane front face. Although the illustration abbreviation was carried out, the film configuration is uniform in the thin long hole 6, and it was checked about other sodium sensor plates of the same lot produced by the same technique that a film configuration is almost the same. If the film configuration is uniform, thickness will also become uniform in each thickness and its variation will decrease.

[0018] The sheet object was further stuck on the above-mentioned levee body 7 of this sodium sensor plate component, the up levee body 9 was formed, and the window parts 9a and 9b corresponding to the above-mentioned crevice and communication hole 9c of a liquid were formed. This completed the differential type sodium ion sensor plate.

[0019] This differential formula sodium ion sensor plate can trickle the standard solution and specimen liquid into each window part 9a and 9b, and can acquire the output value according to that content ion concentration difference by connecting the electrode of the silver larer which carried out [above-mentioned] exposure further to the output circuit equipment which carried out the illustration abbreviation. When the reagent solution of the same concentration (sodium ion concentration $[Na^+] = 140mM$) was dropped at the window parts 9a and 9b of this differential type sodium ion sensor plate and the variation in an output value (ΔE , ideally $\Delta E = 0$) was measured, the probability used as $\Delta E < 0.5mV$ was 90% or more.

[0020] In example of comparison 1 example 1, except not regenerating the ion sensing membrane by THF, sodium ion sensor plate components were produced similarly, and the differential type sodium ion sensor plate was similarly produced using this. The photograph of the front face of the ion sensing membrane of sodium ion sensor plate components is shown in drawing 5 . This photograph shows that irregularity is in an ion sensing membrane locally. And the configuration of the ion sensing membrane which irregularity was seen also about the part which carried out the illustration abbreviation in the thin long hole 6, and was formed in the thin long hole 6 was not uniform. Moreover, the film configuration is scattering about other sodium ion sensor plates of the same lot produced by the same technique, and the identity of a configuration was not seen. The probability set to $\Delta E < 0.5mV$ when ΔE is measured like [plate / differential / type sodium ion sensor] an example 1 was 50% or more.

[0021] Sodium ion sensor plate components were produced like example 2 example 1, this was put in into 100-degree C oven, and the sodium ion sensing membrane was fused with heat. For fully fusing, it required for 15 minutes so that the surface state of an ion sensing membrane might be improved. It took out from oven after this, natural radiationnal cooling was carried out, and the sodium ion sensing membrane was reproduced. Thus, the photograph of the obtained sodium ion sensing membrane front face is shown in drawing 4 . This photograph shows that there is no irregularity in a sodium ion sensing membrane front face. Although the illustration abbreviation was carried out, the film configuration is uniform in the thin long hole 6, and it was checked about other sodium sensor plates of the same lot

produced by the same technique that a film configuration is almost the same. When the differential type sodium ion sensor plate was produced like the example 1 after this and ΔE was measured, the probability used as $\Delta E < 0.5\text{mV}$ was 90% or more.

[0022] Although the above used the same solvent as the ingredient solution of an ion sensing membrane, you may be the solvent which can dissolve an ion sensing membrane, and the solvent which can be swollen, and more than one may be mixed and a solvent may be used. Moreover, the temperature of the glass transition temperature of an ion sensing membrane, softening temperature, and not only melting temperature but others is sufficient as heat-treatment, if temperature is low, time amount will be required, but if temperature is high, generally it can say time amount being short and ending.

[0023] Although the above described the sodium ion sensing membrane as an example, it can say that the same is said of chemistry induction film [, such as an ion sensing membrane of other type,], such as a potassium, calcium, magnesium, and hydrogen ion induction film.

[0024]

[Effect of the Invention] Since according to this invention leave the chemistry induction film and it was made to reproduce in the solvent ambient atmosphere which makes the chemistry induction film dissolve or swell, or the chemistry induction film was heat-treated and it reproduced That film configuration can be made almost uniform among other chemistry induction film which could make the film configuration uniform into the chemistry induction film of one sheet, and was formed using the same technique, and variation in the output value of the chemical sensor using this chemistry induction film can be lessened. Thereby, the yield of a product can be raised.

[Translation done.]